LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

UCRL-CONF-200080

SPUTTER DEPOSITION OF POROUS NANOSTRUCTURED METALS AND NANOSTRUCTURED MEMBRANES FOR CATALYSIS

A. F. Jankowski, J. L. Ferreira, J. P. Hayes

September 18, 2003

204th Meeting of The Electrochemical Society
Orlando, FL, United States
October 12, 2003 through October 16, 2003

Disclaimer

Introduction

The sputter deposition process can be used to create *nano*structured materials that possess continuous open porosity. Characterization of sputter deposited metals and metal-oxide coatings are presented.

Part 1 – Porous *Nano*structured Metals

Porous films are of interest in several electrochemical systems, as in polymer exchange membrane and solid-oxide fuel cells. Thin film fuel cells by *micro*fabrication processes have progressed to demonstration.[1,2] Porous thin films are used to reform hydrocarbon fuels and to function as conductive electrodes. For catalytic functions, in particular, the control of a three-dimensional structure at the *nano*scale provides the means to produce materials with an ideal surface area to volume ratio. A ratio much greater than found in materials as produced by either conventional powder processing or as produced using photolithographic patterning and etching.[3]

Recently, a physical vapor deposition method has been developed to produce metallic films with continuous open porosity at the *nano*scale.[4] The experimental parameters needed to control the porous *nano*structure are found to be tractable and generic for many metals. In general, structural morphologies found for conventionally sputtered coatings can range from porous columnar to dense polycrystalline. The transition in morphology through four zones of growth occurs with increasing substrate temperature and sputter gas pressure. Zone 1 has a structure consisting of tapered crystallites separated by voids. A transition Zone T has a structure consisting of densely packed fibrous grains and a smooth surface. Zone 2 features continuous columns from the substrate to a surface characterized by crystalline facets. Lastly, Zone 3 represents the recrystallized grain structure. The primary effect of increased temperature is an enhancement of surface and bulk diffusion.

A new growth zone for the stabilization of a porous *nano*structure is seen as a variant of Zones T and 2.[4] A three-dimensional polycrystalline deposit with continuous open porosity is produced under the general conditions of an increased working gas pressure and a substrate temperature approximately half the absolute melting point. The open-porosity morphology is demonstrated in as-deposited *nano*structures of nickel.[4] New results are presented for copper – a base metal used in several catalytic materials for the direct reformation of methanol. The use of a moderate sputter gas pressure and an elevated substrate temperature yields a *nano*structured metal with open porosity, i.e. *a metallic sponge*. The moderate sputter gas pressure creates a range of incident angles for deposition and the elevated temperature promotes a faceted crystalline growth. Results for a 5 μm thick copper coating are seen in plan view (Figs. 1-2) and cross-section (Figs. 3-4). Of interest, is the coarsening in grain size that occurs from the substrate through the cross-section to the surface.

Part 2 – *Nano*structured Membranes for Catalysis

Porous films in the form of *nano*structured membranes are of interest in several electrochemical systems, as for use as electrodes in polymer exchange membrane and solid-oxide fuel cells. Over the past decade, solid-oxide fuel cells produced by sputter deposition as thin film layered structures [2,5] have progressed from a one milliamp output at 300 ºC to demonstration as *micro*fuel cell devices [6] capable of providing an output power at 600 ºC of several hundred milliwatts per square centimeter. More recently, sputter-deposited porous membranes have generated interest for use in *micro*fuel cells as electrodes [4,6] (Fig. 5) and as catalysts to reform hydrocarbons as methanol.

*Nano*structured membranes for catalytic functions, in particular, require optimization of a three-dimensional structure to provide functional materials with an ideal surface area to volume ratio. The *nano*structured membrane can potentially yield a much greater ratio than found in materials as produced by either conventional or unconventional powder processing [5] or as produced by using photolithographic patterning and etching [2]. Recently, through the development of a physical vapor deposition method [4], metallic membranes have been produced with continuous open porosity at the *nano*scale. The experimental parameters needed to control the porous *nano*structure are found to be tractable and generic for many metals including gold, silver, nickel, and aluminum.[4]

The result presented for depositing porous *nano*structured copper (Fig. 4) provides the basis for synthesizing copper alloys that are of interest for use as catalytic materials. Specifically, copper-zinc-oxide is a known oxide compound widely used for the direct reformation of hydrocarbon fuels at low temperatures. A porous *nano*structure is found in a several-micron thick copper-zinc-oxide coating, sputter deposited from a copper-zinc alloy target using a partial pressure of oxygen, as shown in a scanning electron microscopy (SEM) image (Fig. 6). The analysis of an energy dispersive spectrometry (EDS) scan that corresponds with this coating reveals the composition to be Cu-19%Zn-14%O.

Summary

Sputter deposition is a method used to prepare *nano*structured metals and membranes with continuous open porosity. Examples are shown in applications as electrode and as catalytic membranes for energy conversion *micro*devices. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

References

1. A.F. Jankowski and J.D. Morse, *MRS Symp. Proc. 496 (1998) 155*.

2. A.F. Jankowski, R.T. Graff, J.P. Hayes, and J.D. Morse, *ECS Proc. 99-19 (1999) 932*.

3. J.D. Morse, et al., *MRS Symp. Proc. 575 (2000) 321*.

4. A.F. Jankowski and J.P. Hayes, *J. Vac. Sci. Technol. A 21 (2003) 422*.

5. A.F. Jankowski, *ECS Proc. 97-24 (1997) 107*.

6. A.F. Jankowski, J.P. Hayes, R.T. Graff, and J.D. Morse, *MRS Symp. Proc. 730 (2002) 93.*

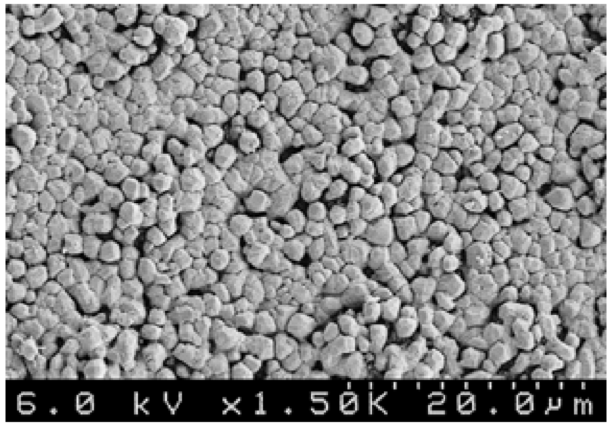


Fig. 1. The plan view image of copper produced from deposition at high temperature and sputter gas pressure.

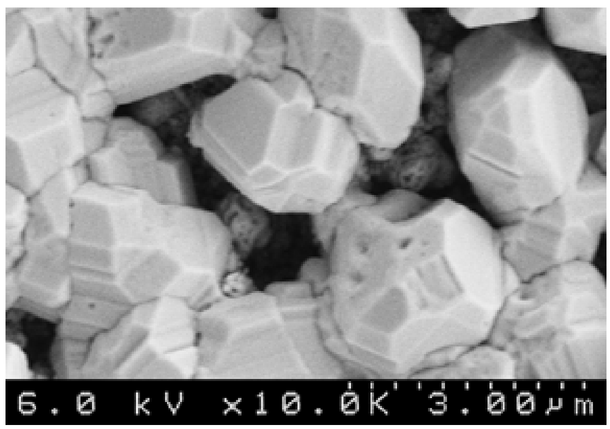


Fig. 2. A high-magnification plan view image (of Fig. 1) shows the open porosity of the porous copper coating.

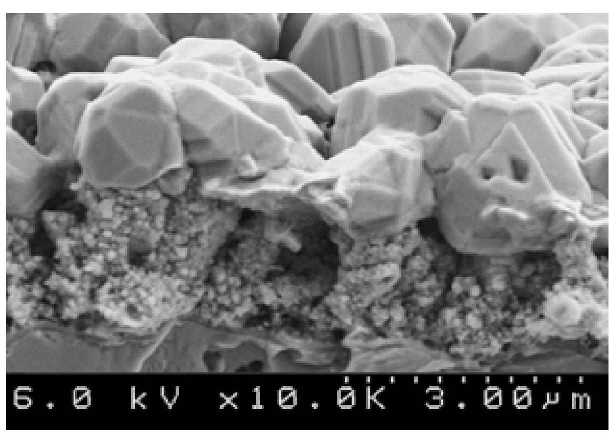


Fig. 3. A fracture cross-section shows the coarsening in crystal size through the porous copper coating.

Fig. 4. A higher magnification view (of Fig. 3) reveals the porous assembly of copper nanocrystals that forms at the base of the sputter deposited coating.

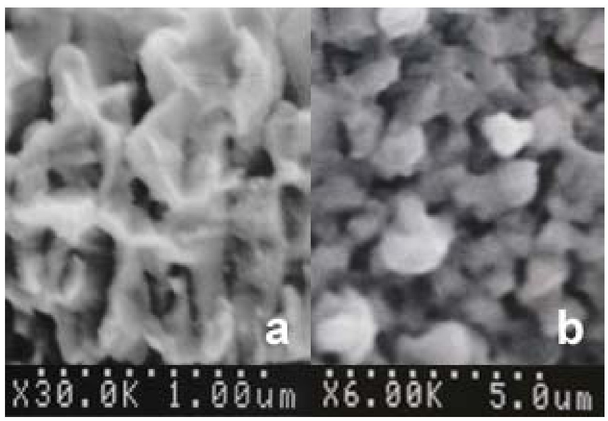


Fig. 5. SEM images of porous electrodes of (a) Ni, viewed in cross-section, and (b) Ag, in plan view, that were deposited at high temperature and sputter gas pressure.

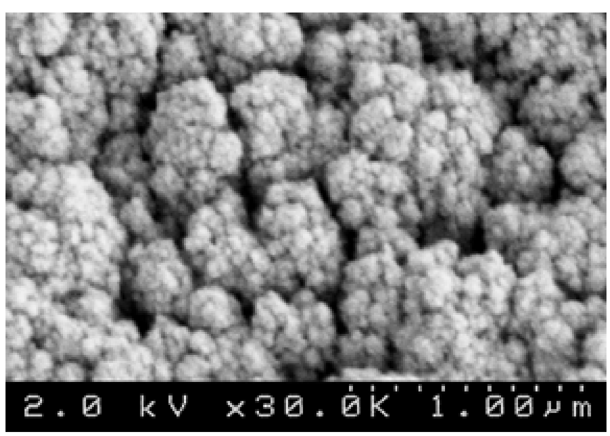
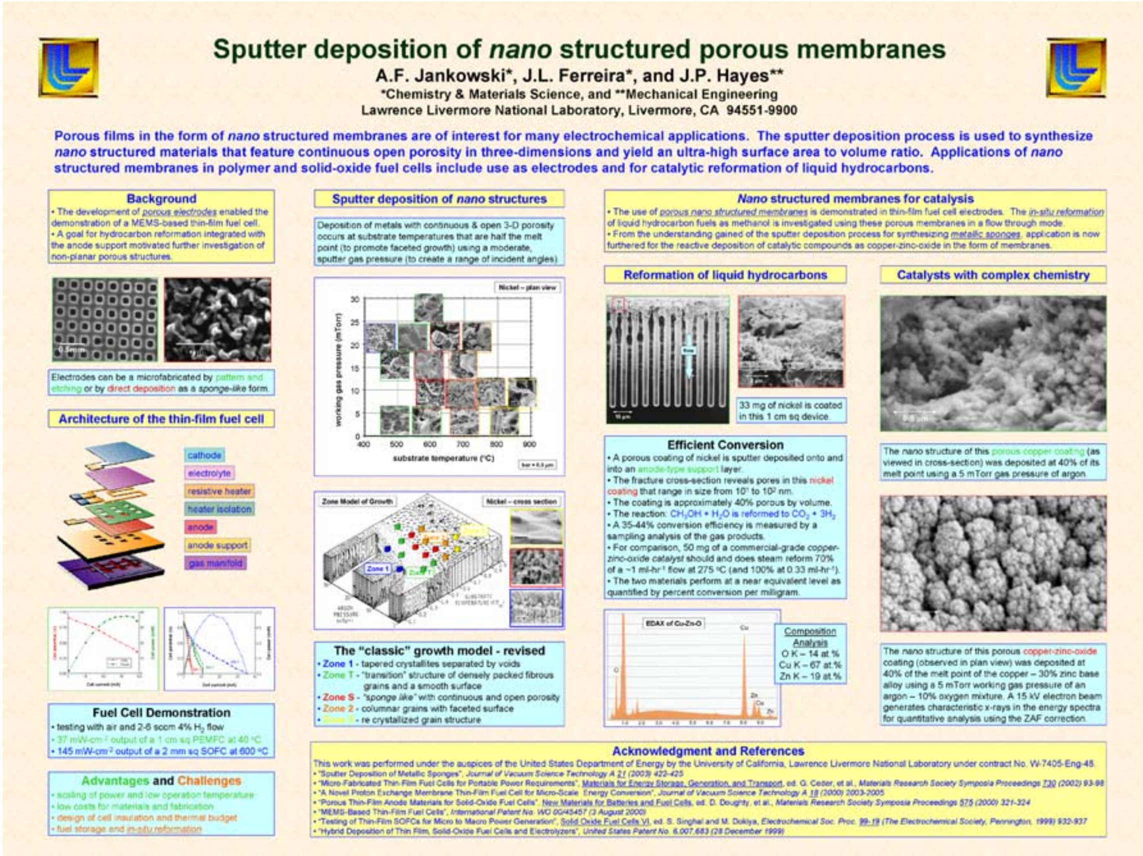


Fig. 6. SEM image of a Cu-Zn-O porous membrane, in plan view, that was reactively sputter deposited for use in catalytic hydrocarbon reformation.



Sputter deposition of nano structured porous membranes
A.F. Jankowski*, J.L. Ferreira*, and J.P. Hayes**
*Chemistry & Materials Science, and **Mechanical Engineering
Lawrence Livermore National Laboratory, Livermore, CA 94551-9900
Porous films in the form of nano structured membranes are of interest for many electrochemical applications. The sputter deposition process is used to synthesize nano structured materials that feature continuous open porosity in three-dimensions and yield an ultra-high surface area to volume ratio. Applications of nano structured membranes in polymer and solid-oxide fuel cells include use as electrodes and for catalytic reformation of liquid hydrocarbons.
Background
• The development of porous electrodes enabled the demonstration of a MEMS-based thin-film fuel cell.
• A goal for hydrocarbon reformation integrated with the anode support motivated further investigation of non-planar porous structures.
Electrodes can be a microfabricated by pattern and etching or by direct deposition as a sponge-like form.
Architecture of the thin-film fuel cell
cathode
electrolyte
resistive heater
heater isolation
anode
anode support
gas manifold
Fuel Cell Demonstration
• testing with air and 2-6 sccm 4% H_2 flow
• 37 mW-cm^{-2} output of a 1 cm sq PEMFC at 40 °C
• 145 mW-cm^{-2} output of a 2 mm sq SOFC at 600 °C
Advantages and Challenges
• scaling of power and low operation temperature
• low costs for materials and fabrication
• design of cell insulation and thermal budget
• fuel storage and in-situ reformation
Sputter deposition of nano structures
Deposition of metals with continuous & open 3-D porosity occurs at substrate temperatures that are half the melt point (to promote faceted growth) using a moderate, sputter gas pressure (to create a range of incident angles)
Nickel – plan view
working gas pressure (mTorr)
substrate temperature (°C)
Zone Model of Growth
Nickel – cross section
Zone 1
The "classic" growth model - revised
• Zone 1 - tapered crystallites separated by voids
• Zone T - "transition" structure of densely packed fibrous grains and a smooth surface
• Zone S - "sponge like" with continuous and open porosity
• Zone 2 - columnar grains with faceted surface
• Zone 3 - re crystallized grain structure
Nano structured membranes for catalysis
• The use of porous nano structured membranes is demonstrated in thin-film fuel cell electrodes. The in-situ reformation of liquid hydrocarbon fuels as methanol is investigated using these porous membranes in a flow through mode.
• From the understanding gained of the sputter deposition process for synthesizing metallic sponges, application is now furthered for the reactive deposition of catalytic compounds as copper-zinc-oxide in the form of membranes.
Reformation of liquid hydrocarbons
33 mg of nickel is coated in this 1 cm sq device.
Efficient Conversion
• A porous coating of nickel is sputter deposited onto and into an anode-type support layer.
• The fracture cross-section reveals pores in this nickel coating that range in size from 10^1 to 10^2 nm.
• The coating is approximately 40% porous by volume.
• The reaction: $CH_3OH + H_2O$ is reformed to $CO_2 + 3H_2$
• A 35-44% conversion efficiency is measured by a sampling analysis of the gas products.
• For comparison, 50 mg of a commercial-grade copper-zinc-oxide catalyst should and does steam reform 70% of a ~1 ml-hr^{-1} flow at 275 °C (and 100% at 0.33 ml-hr^{-1}).
• The two materials perform at a near equivalent level as quantified by percent conversion per milligram.
EDAX of Cu-Zn-O
Composition Analysis
O K – 14 at.%
Cu K – 67 at.%
Zn K – 19 at.%
Catalysts with complex chemistry
The nano structure of this porous copper coating (as viewed in cross-section) was deposited at 40% of its melt point using a 5 mTorr gas pressure of argon.
The nano structure of this porous copper-zinc-oxide coating (observed in plan view) was deposited at 40% of the melt point of the copper – 30% zinc base alloy using a 5 mTorr working gas pressure of an argon – 10% oxygen mixture. A 15 kV electron beam generates characteristic x-rays in the energy spectra for quantitative analysis using the ZAF correction.
Acknowledgment and References
This work was performed under the auspices of the United States Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.
• "Sputter Deposition of Metallic Sponges", Journal of Vacuum Science Technology A 21 (2003) 422-425
• "Micro-Fabricated Thin-Film Fuel Cells for Portable Power Requirements", Materials for Energy Storage, Generation, and Transport, ed. G. Ceder, et al., Materials Research Society Symposia Proceedings 730 (2002) 93-98
• "A Novel Proton Exchange Membrane Thin-Film Fuel Cell for Micro-Scale Energy Conversion", Journal of Vacuum Science Technology A 18 (2000) 2003-2005
• "Porous Thin-Film Anode Materials for Solid-Oxide Fuel Cells", New Materials for Batteries and Fuel Cells, ed. D. Doughty, et al., Materials Research Society Symposia Proceedings 575 (2000) 321-324
• "MEMS-Based Thin-Film Fuel Cells", International Patent No. WO 00/45457 (3 August 2000)
• "Testing of Thin-Film SOFCs for Micro to Macro Power Generation", Solid Oxide Fuel Cells VI, ed. S. Singhal and M. Dokiya, Electrochemical Soc. Proc. 99-19 (The Electrochemical Society, Pennington, 1999) 932-937
• "Hybrid Deposition of Thin Film, Solid-Oxide Fuel Cells and Electrolyzers", United States Patent No. 6,007,683 (28 December 1999)